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THERMOCHEMISTRY OF OXYGEN-FLUORINE BONDING

Research Division

UNITED TECHNOLOGY CORPORATION
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FIRST QUARTERLY TECHNICAL SUMMARY REPORT
CONTRACT NO. Nonr 3433(00)

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FIRST QUARTERLY TECHNICAL SUMMARY REPORT
FOR PERIOD CLOSING 30 JUNE 1961
Under Contract No. Nonr 3433 (00)

Propulsion Chemistry Branch
Material Sciences Division
Office of Naval Research

ARPA ORDER No. 184-61
(This project is financially supported by the
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ABSTRACT

The objective of the research program under Contract Nonr 3433(00) can be represented briefly as follows:

> Determination of reliable thermochemical data pertaining to fluorine bonding
>
> Ascertaining effects of substituents on the stability of the O-F group to evaluate the relative stabilities of hypothetical structures with O-F bonding.

The major effort during this first report period was concentrated on design, fabrication, and procurement of the experimental equipment requisite to synthesis of oxygen - fluorine compounds and compositional analysis of reaction products for thermochemical evaluation of synthesized materials. Reaction systems have been constructed for synthesis and purification of NO_2F, NO_3F, and ClO_4F.

Synthesis of NO_2F has been accomplished directly from NO_2 and F_2. The synthesized material has been analyzed for purity by infrared spectroscopy, mass spectroscopy, and by hydrolysis. The two latter techniques of analysis agree within one percent.

A calorimeter for the heat-of-formation reaction of $NO_2 + F_2$ is presently under construction.

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LIST OF FIGURES

I. INTRODUCTION

This is the first in a series of Technical Quarterly Reports issued in partial fulfillment of Contract Nonr 3433 (00). The project period covered herein was extended to four months in adjusting the documentation schedule to the instructions received in the latter part of June 1961.* The second Technical Quarterly Report will cover the months of July, August, and September in normal reporting procedure.

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* Letter reference ONR: 426 : RR : BG, NR 093-020a, dated 22 June 1961.

II. TECHNICAL ACTIVITY

2.1 OBJECTIVES OF THE PERIOD REPORTED

The specific objectives of the experimental work performed during this first report period have been the following:

A. Design, fabrication, and procurement of necessary experimental equipment for synthesis of NO_2F, NO_3F, and ClO_4F.

B. Development of consistent analytical techniques for determination of reaction products. These techniques include mass spectroscopy, gas chromatography, hydrolysis, purification by fractional distillation, and infrared spectroscopy.

C. Design and fabrication of suitable calorimeters for measurement of the heats of reaction for NO_2F, NO_3F, and ClO_4F.

D. Synthesis and purification of NO_2F from elemental fluorine and nitrogen dioxide.

2.2 STUDY OF NO_2F

2.2.1 Synthesis

Figure 1 is a photograph of the assembled experimental system. The NO_2F synthesis system is depicted schematically in Figure 2.

The synthesis of NO_2F from F_2 and NO_2 by the reaction $NO_2 + 1/2\ F_2 = NO_2F$ is carried out in the following manner:

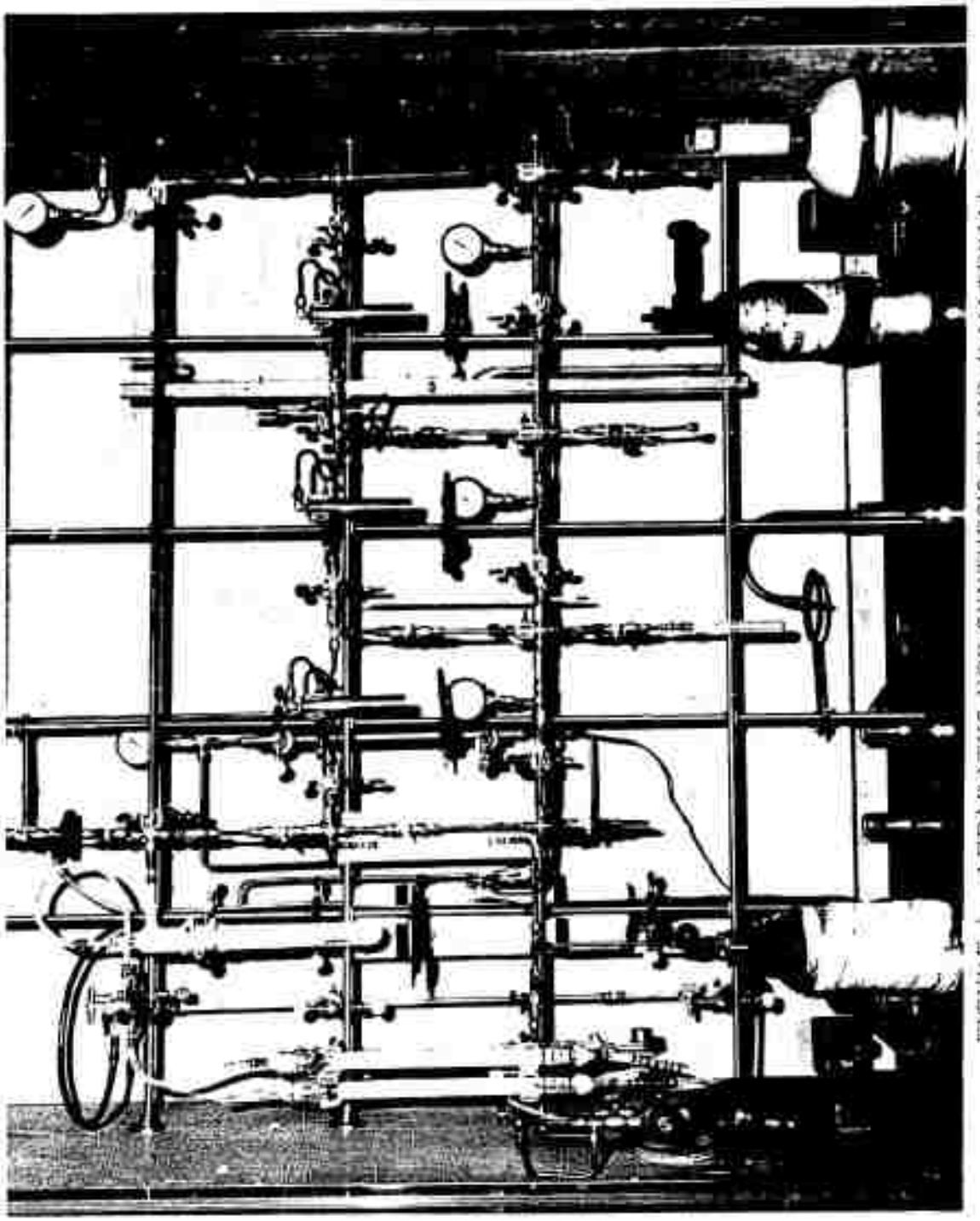

FIGURE 1. APPARATUS FOR SYNTHESIS OF NO_2F MATERIAL

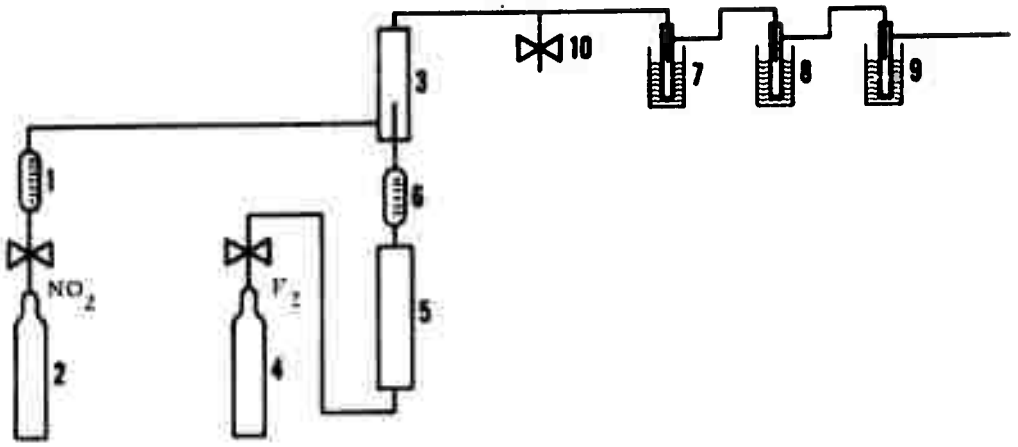

FIGURE 2. SCHEMATIC DIAGRAM OF SYSTEM FOR NO_2F SYNTHESIS

Refer to numbered callouts in Figure 2. Pure gaseous NO_2 at room temperature is metered by flowmeter (1) from the reserve tank (2) into the reactor (3). Fluorine from the reserve tank (4) is scrubbed in a sodium fluoride column (5) to remove any residual HF and metered by flowmeter (6) into the reactor (3). The synthesized NO_2F and other reaction products from the reactor are permitted to flow through a series of cold traps (7, 8, and 9). The traps are at different temperatures for purification purposes. The reaction products for analysis are taken directly from the exit end of the reactor (at port 10). Samples are taken in separate cylinders fabricated of nickel or Monel for each type of analysis. Also, the entire reaction system is fabricated of nickel, Monel, and copper.

2. 2. 2 Analyses

A. The mass spectrometric analyses are made on a CEC mass spectrometer that has been conditioned specifically for analysis of fluorine compounds. These analyses are performed for United Technology Corporation by Stanford Research Institute.

B. The infrared measurements are made on a Beckman IR- 7 infrared spectrophotometer. A special gas cell fabricated of Monel and equipped with BaF_2 windows is used for all the infrared measurements.

C. A special hydrolysis system has been constructed to meet the requirements of these reactive materials. The system is fabricated of glass and the glass is coated with an inert wax to prevent absorption and decomposition of the materials to be analyzed. The technique for this analysis has been worked out previously. *

D. Measurements by gas chromatography are being obtained with a unit of the conventional type. The inert packing is Kel-F powder and Kel-F oil is used as the liquid phase. This combination is moderately inert with respect to the materials being studied and appears to give adequate separation.

2. 2. 3 Heat of Formation - Calorimetry

The heat of formation of NO_2F will be measured directly from the synthesis of NO_2F from NO_2 and F_2. As NO_2 and F_2 are gases at

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* Moissan and Lebeu, Ann. Chim. Phy., 8, 9, 226.
Ruff, Menzel, and Neumann, Z. Anorg. Chem., 203, 302 (1932).

ambient temperatures, a flow calorimeter can be applied directly. As soon as the composition of the reaction products can be established with a high degree of certainty, calorimetric measurements of the heat of reaction (in this case heat of formation of NO_2F) will be obtained. The flow calorimeter to be used is shown schematically in Figure 3.

For accurate calorimetric measurements with a flow type of calorimeter, it is imperative to have constant and reproducible reactant flows. To accomplish this, a constant pressure head is maintained in the reactor (1) with precision Grove reducing regulators (2 and 3) (specially fabricated) in the feed lines and a Grove back-pressure regulator (4) at the exit of the calorimeter. The amount of F_2 discharged into the calorimeter is determined by the pressure drop in the supply cylinder (5) as a function of time. Such is not possible for NO_2 because NO_2 has only a small vapor pressure at ambient

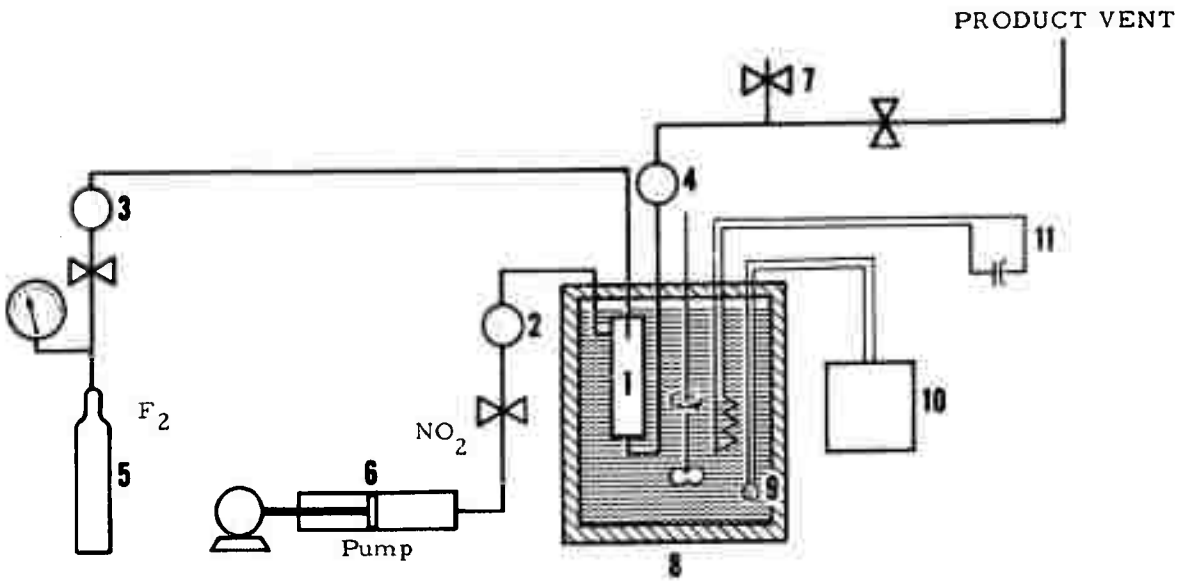


FIGURE 3. SCHEMATIC DIAGRAM OF FLOW-CALORIMETER SYSTEM

temperatures. The constant flowrate of NO_2 is obtained by use of a constant drive piston pump (6). The reaction products are sampled (at 7) directly downstream from the back-pressure regulator (4).

The reaction vessel (1) is enclosed in a one-gallon Dewar flask (8) and is immersed completely in water. The water acts as the heatsink fluid. The heat generated in the formation of NO_2F in the reactor is dissipated to the surrounding heatsink fluid. The temperature change of the system is measured with a precision resistance thermometer (9) and Mueller bridge assembly (10). The heat capacity of the system is determined electrically with a calibration heater (11).

The results provide sufficient data for deriving the heat of formation.

2.2.4 Measurement of Physical Properties

When sufficient material has been synthesized and purified, the vapor pressures will be measured. Measurements will be obtained through use of an isoteniscope specifically designed for reactive materials. The apparatus consists essentially of a bellows pressure transmitter. This assembly permits an accuracy in pressure measurements to greater than 0.1 mm.

A system is now being fabricated for density determinations.

2.3 STUDY OF NO_3F AND ClO_4F

2.3.1 Synthesis

The system designed for NO_3F and ClO_4F is shown schematically in Figure 4. Figures 5, 6, and 7 are photographs of the fabricated

system. Inasmuch as materials are inherently unstable, the syntheses are performed by semiremote control in explosion-proof facilities. Initially, NO_3F and ClO_4F will be synthesized from concentrated nitric and perchloric acids, respectively, and fluorine gas. A constant-flow piston pump (1) will supply the concentrated acids to the reactor (2). As the reaction is expected to be quite exothermic, the reactor is continuously cooled in a constant-temperature bath (3). The F_2 is metered from the reserve tank (4) by the flowmeter (5) into the reactor (2). The products then flow through a number of Kel-F traps (6, 7, and 8). The traps are maintained at various temperatures to facilitate purification of the synthesized material. This equipment is ready for initial synthesis trials.

2. 3. 2 Analyses

The NO_3F and ClO_4F will be analyzed with methods similar to

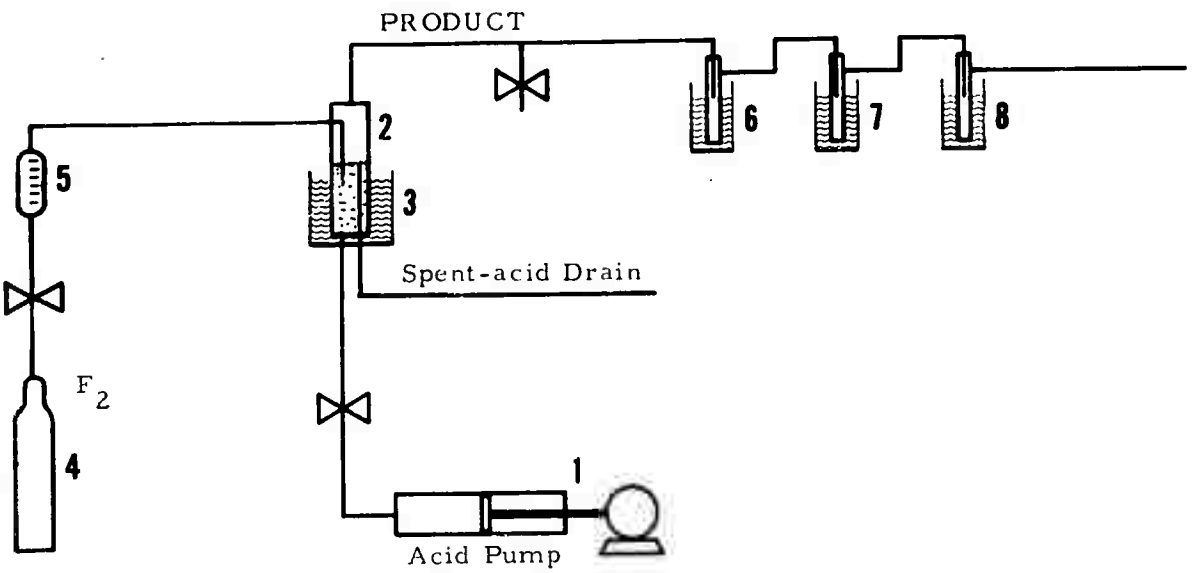


FIGURE 4. SCHEMATIC DIAGRAM OF SYSTEM FOR NO_3F AND ClO_4F SYNTHESIS

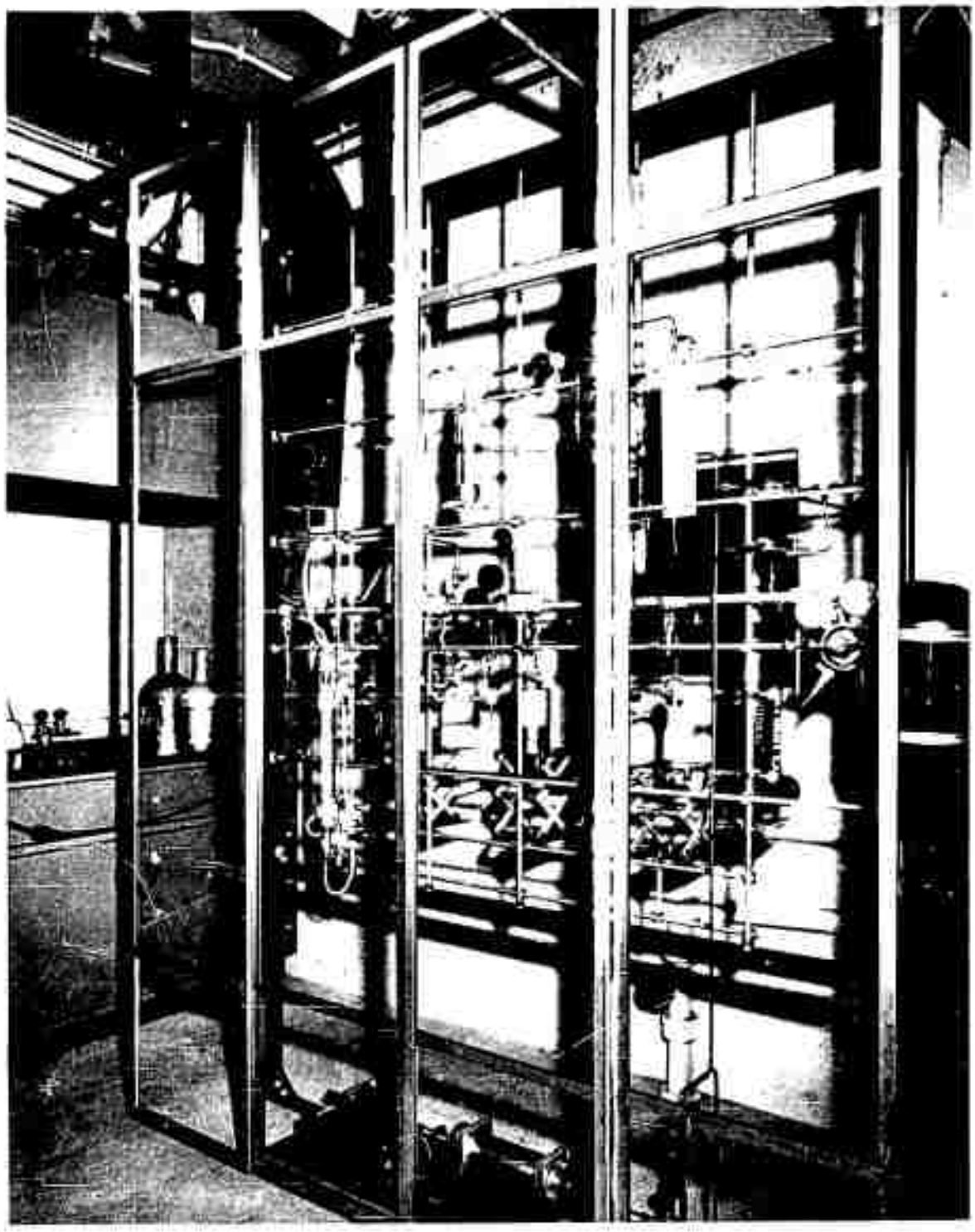
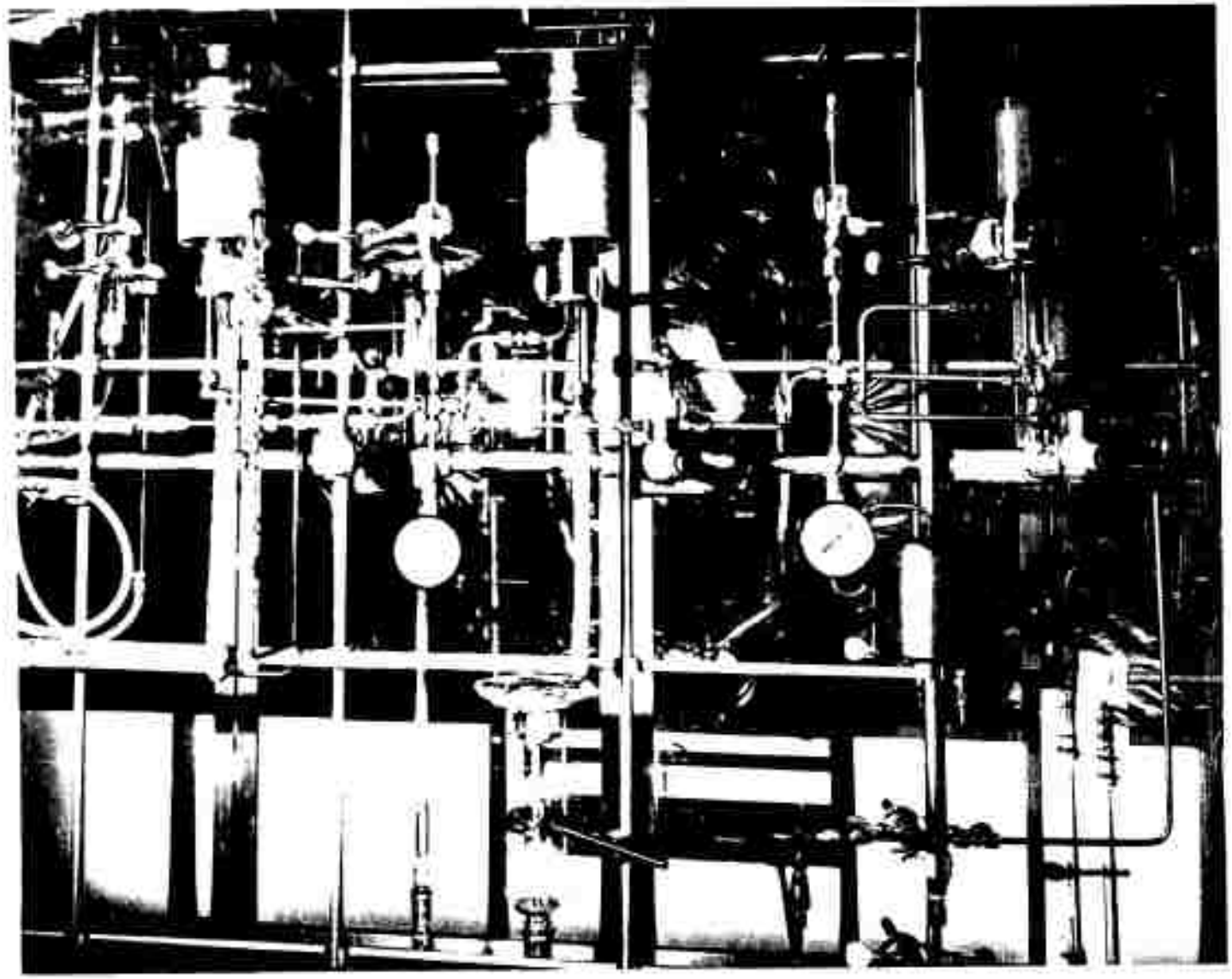


FIGURE 5. APPARATUS FOR SYNTHESIS OF NO_3F AND ClO_4F MATERIALS



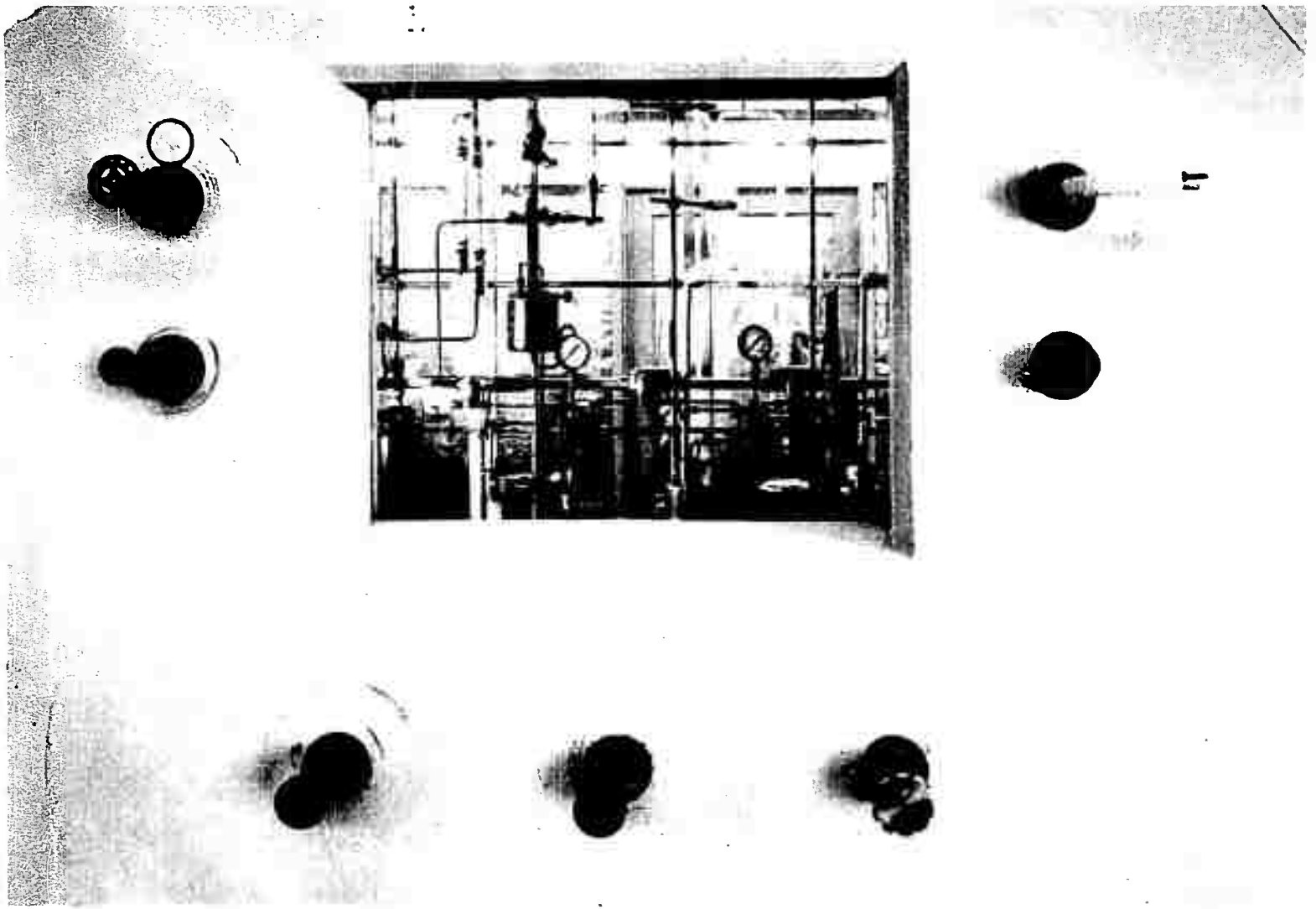


FIGURE 7. APPARATUS FOR SYNTHESIS OF NO_3F AND ClO_4F AS SEEN THROUGH LABORATORY WINDOW

those used for NO_2F. The problems of analysis are expected to be parallel.

2. 3. 3 Calorimetric Measurements

The calorimeter for these two reaction systems is presently being designed. The calorimeter will be of the flow type and similar to the NO_2F calorimeter.

2. 3. 4 Measurement of Physical Properties

The vapor pressures and densities of NO_3F and ClO_4F will be determined when sufficient material has been synthesized and purified.

III FUTURE WORK

Synthesis, analysis, and purification of NO_2F will be continued to provide quantitative information on the $NO_2 + F_2$ reaction. The calorimetric studies will be initiated upon satisfactory resolution of the reaction products.

The materials NO_3F and ClO_4F will be synthesized and the composition of the reaction products will be established. The calorimetric studies for derivation of the heat of formation of these compounds will be initiated as soon as the products of the reaction are known with sufficient accuracy.

Vapor pressures and densities will be measured for NO_2F, NO_3F, and ClO_4F.

There will be a theoretical correlation of these data to obtain reliable information on the stability and thermodynamic properties of O-F bonded compounds.